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Hysteresis of the magnetic properties of soft magnetic gels

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We present results of an experimental and theoretical study of the magnetic properties of soft magnetic gels consisting of micron-sized magnetizable particles embedded in a polymer matrix. Experiments demonstrate hysteretic dependences of composite magnetization on an applied magnetic field and non-monotonic, with maximum, dependence of the sample susceptibilities on the field. We propose a theoretical approach which describes the main physical features of these experimental results.

I. Introduction

Composites of fine, nano- or micron-sized, magnetic particles in polymeric matrices present a new kind of magnetically controlled soft materials, usually named as ferrogels, ferroelasts, magnetically active elastomers, *etc.* These systems have attracted considerable interest from researchers and engineers due to the rich set of physical properties valuable for many industrial and bio-medical applications.[1–5]

Experiments demonstrate strong hysteretic effects in ferrogels with the soft matrix filled by the micron-sized magnetizable particles (see, for example, ref. 6–8) as, the wide hysteresis loops of the stress–strain dependence have been observed in ferrogels placed in a uniform magnetic field.[7] In contrast, the linear stress–strain dependence was detected in ref. 6 for the same samples in experiments without the field.

Hysteretic dependence of the gel magnetostriction (elongation under the field action) has been detected in ref. 6–8. The similar shape of the curves of the sample magnetization *vs.* applied magnetic field has been observed in ref. 7. Remarkably hysteresis of magnetization has not been observed for the dry powder of the magnetic filler; for the ferrogels the area of the hysteresis loops increased with the decrease of the elastic modulus of the sample.

The last results show that the physical cause of the hysteresis effects can lie only in the rearrangement of the particles in the soft matrix. Indeed, observations of ref. 7 show that the initially randomly distributed particles, under the field action, unite into the chain-like aggregates.

Unification of the particles into the chains and other aggregates in liquid magnetic suspensions is a well-known phenomenon, which has been reported in many studies(see, for example, overviews in ref. 9 and 10). However, to the best of our knowledge, the magnetically induced rearrangement of the particles in an elastic matrix; formation of the internal heterogeneous structures as well as the effect of these structures on macroscopic properties of the soft magnetic composites have not been studied yet in the literature. At the same time, these phenomena present significant interest both from the scientific point of view and from the viewpoint of practical applications of the mechanically soft magnetic materials.

In this paper we suggest a simple model of formation of the chain-like structures in a system of magnetizable particles embedded in a soft elastic matrix and estimate the effect of these structures on the magnetic properties of these composites. Theoretical results are compared with the measurements of magnetization and susceptibility of the soft ferrogels. Both theory and experiments demonstrate the hysteretic dependences of the composite magnetic properties on the applied field. Theoretical results are in agreement, at least in the order of magnitudes, with the experimental ones.

The structure of this work is as follows. In the Section II we describe the experiments on the measurements of the magnetic properties of the soft magnetic gels. The theoretical model is described in the Section III. In Section IV we compare and discuss the experimental and theoretical results.

II. Experiment

Considered in this study that ferrogel samples are based on a polydimethylsiloxane (PDMS) matrix, which is polymerized

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using an organometallic cross-linking agent in a way similar to the one published elsewhere.[7,11] Particles of the magnetic powder were embedded in the liquid matrix under mechanical stirring. Further the mixture was degassed in a vacuum chamber following polymerization in a mould under applied heat (120 °C). The high temperature is applied in order to accelerate the polymerization process of the matrix. As a magnetic filler carbonyl iron particles BASF CC with a spherical shape and a mean diameter of about 5 micrometers were used. The volume concentrations of the powder in the composite samples were 0.058 and 0.167.

The elastic modulus of the matrix was evaluated using customized table-top machine Dyna-Mess within a conventional axial compression of the cylindrical samples at a low strain (<5% of deformation). The machine allows the measuring of forces and displacements which are further transformed into stress and strain values, respectively, taking into account the geometry of the sample. The class of accuracy for both the load cell and displacement transducer is 0.1, and the best possible resolution for the measurements is 0.01 N and 0.01 mm, respectively. Measured force-displacement and consequent stress–strain curves are linear and the elastic modulus of the matrix obtained by this method is E = 20 kPa.

The manufactured samples were characterized using vibrating sample magnetometer Lake Shore 7404 for the magnetic measurements. In this experiment the magnetic moment is measured by vibrating the sample perpendicular to an externally applied uniform magnetic field in between a set of pickup coils. The device is calibrated using a spherical reference sample made of Ni and a resolution of $\sim 10^{-9}$ A m^2 to measure the magnetic moment m is provided. The magnetization is determined as $M = m/V$, where V represents the sample volume and, herewith, a second source of uncertainty is introduced. Obviously, an uncertainty about the sample volume does not match the resolution of the magnetic moment measurements. However, a resulting accuracy of 1 A m^{-1}, which can be easily provided, is high enough compared to magnetization of the MR composite. Results of magnetic measurements are presented in Fig. 7–10. Generally, used powder, which is magnetically soft carbonyl iron, is considered to be a material without magnetic hysteresis. Nevertheless, the measured composite magnetization M in the decreasing magnetic field H is higher than the magnetization in the increasing field. The same is consequently observed for the differential susceptibility $\chi_d = dM/dH$. This effect can be accounted for by the mobility of the particles and structure formation of the particles in a soft elastic matrix.[7]

III. Theory

In this part we propose a theoretical model for explanation of the experimentally observed hysteretic behavior (Fig. 7–10) of the magnetization of gels as well as of the maxima of the composite susceptibility (Fig. 9 and 10).

Unification, under the field action, of the particles into chains is a result of competition between the magnetic attraction of the particles on the one hand, and the matrix elastic resistance to the particle displacement, on the other hand. That is why, first, we will estimate the elastic and magnetic forces, acting on the particles in the soft matrix.

III.1 Elastic forces

Let us consider a magnetic gel, consisting of identical spherical micron-sized magnetizable particles embedded in an incompressible gel matrix. We suppose that the matrix was cured without a magnetic field; the particles, initially, are uniformly distributed in the gel. Our first goal is to describe unification of the particles, under the magnetic field action, into the linear chain-like aggregates.

For maximal simplification of the mathematical part of the problem, we will use the main ideas of the hierarchical model[12] of the chain formation in magnetorheological suspensions, combined with the lattice model, often used in the statistical physics of gas and liquid systems.[13]

In the framework of the lattice approach, we will suppose that initially the particles are situated in the centers of cells of a cubic lattice (Fig. 1). Let one of the lattice axes be directed along the applied magnetic field H_0.

We estimate the edge l of the cubic cell by using the condition that the particle volume concentration in the lattice model is equal to the concentration φ of the particles in the real composite. This gives:

$$\frac{v_p}{l^3} = \varphi \text{ or } l = a\left(\frac{4\pi}{3\varphi}\right)^{\frac{1}{3}}. \quad (1)$$

Here $v_p = 4\pi a^3/3$ is the particle volume, a is the particle radius.

For further consideration it is convenient to introduce the dimensionless edge $\tilde{l}$ as:

$$\tilde{l} = \frac{l}{a} = \left(\frac{4\pi}{3\varphi}\right)^{\frac{1}{3}}. \quad (2)$$

Obviously, the condition $\tilde{l} > 2$, which reflects impossibility for the particles to interpenetrate, must be held.

We will take into account interaction only between the particles, situated along the axis, parallel to the applied magnetic field. Analysis shows that the direct application of the lattice model, where the particles are situated right in the centers of the cells, leads to very rough description of the chaining, since this approximation does not take into account the statistical character of the mutual distribution of the particles.

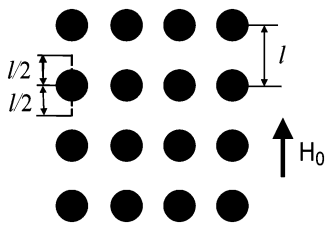

Fig. 1 Sketch of the cubic lattice. Dots present the particles situated at the centers of the lattice cells. A segment of the possible positions one of the particles can occupy is shown in the left part of the lattice.

In order to approach the lattice model to the real systems with the random spatial distribution of the particles, we will suppose that the center of each particle, with equal probability, can be situated in a linear segment, aligned along the field H_0. The length of this segment is $l - 2a$, the segment center coincides with the center of the lattice cell. The situation is illustrated in Fig. 1, where the boundaries of the segment for the particle extremities (poles) are shown.

Following the ideas of the hierarchical theory,[12] we consider the process of the chain formation as the unification of the particles into the doublets; then – unification of the doublets into the "quartets" of the particles, *etc.* Various stages of this unification are illustrated in Fig. 2.

The center of the each doublet can take a place in each point of a segment with the length $2(l - 2a)$, with the center right in the middle between the centers of the cells of the single particles. A similar assumption is made for the centers of the four-particle clusters, and so on (Fig. 2).

In the hierarchical approach each chain consists of $n = 2^k$ particles, where k is the number of the stage of the chaining.

The number of particles in a stable chain is determined by the competition between the forces of magnetic attraction between the particles and the force of elastic stress in the matrix. For maximal simplification of calculations, we apply the linear Hook's law of the matrix elastic deformation.

Let us consider two neighbor chains and denote the number of particles in the chain as j. We suppose that the "lowest" particle in the "upper" chain and the "highest" particle in the "down" chain (see illustration in Fig. 3) have the number 1. Simple calculations show that displacement of the j-th particle right after the chain formation in the upper chain is:

$$\delta z_j^{(0)} = \left(\frac{n+1}{2} - j\right)(l_r - 2a). \tag{3}$$

Here l_r is the random value of the distance between centers of the nearest particles of the neighbor chains. Due to the fact that the chains can be situated in the arbitrary points of their segments, as shown in Fig. 2, the minimum value of this distance is $2a$ (the particles cannot interpenetrate); the maximum value is $2n(l - 2a) + 2a$.

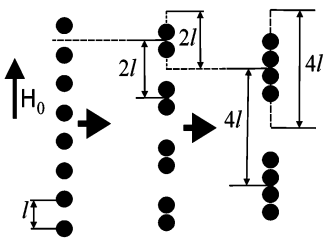

Fig. 2 Sketch of three first stages (I, II, III) of the particle aggregation. The horizontal arrows illustrate evolution of the particles in time. The segments of possible positions of the chains are shown. The segment boundaries are for the poles of the particles at the chain extremities. The single particles and the chains are shown at the centers of the segments of their possible positions.

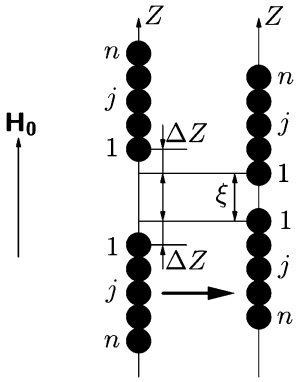

Fig. 3 Illustration of the displacement of chains towards each other. Left – the relative position of the chains immediately after their formation; right – after the displacement. Horizontal arrow – evolution in time.

Let us suppose now that each of these two chains has been displaced (under their magnetic attraction) towards the other one for the distance ΔZ with respect to the position of the chain formation. This situation is illustrated in Fig. 3.

The total displacement of the j-th particle of the upper chain in Fig. 3, with respect to the initial position of the particle shown in Fig. 1, is:

$$\delta z_j = \delta z_j^{(0)} - \Delta Z = \left(\frac{n+1}{2} - j\right)(l_r - 2a) - \Delta Z. \tag{4}$$

Similarly to that, the total displacement of the j-th particle in the lower chain is:

$$\delta z_j = -\delta z_j^{(0)} + \Delta Z = -\left(\frac{n+1}{2} - j\right)(l_r - 2a) + \Delta Z. \tag{5}$$

This is convenient to introduce the distance ξ between the centers of the particles at the nearest extremities of the chains (see Fig. 3). One can easily show that the following relation is held:

$$\xi = n(l_r - 2a) + 2a - 2\Delta Z. \tag{6}$$

The total energy of the matrix deformation, corresponding to the positions of the chains as shown in Fig. 3, in the Hook approximation can be presented as:

$$U_n^{(el)} = \frac{G}{2}\sum_{j=1}^{n}\left[\left(\delta z_j^{(0)} - \Delta Z\right)^2 + \left(\Delta Z - \delta z_j^{(0)}\right)^2\right], \tag{7}$$

where G is a coefficient, to be determined. In the case of an incompressible matrix one can use the well-known similarity between the equation of flow of a Newtonian fluid and the linear deformation of an elastic medium. This leads us to the formula

$$G = 6\pi\mu a,$$

similar to that for the drag coefficient in the Stokes law for the force, acting on a sphere moving in a viscous fluid. Here μ is shear modulus of the matrix.

Let us introduce the dimensionless elastic energy:

$$\tilde{U}_n^{(\mathrm{el})} = \frac{U_n^{(\mathrm{el})}}{Ea^3} \tag{8}$$

where $E = 3\mu$ is the Young's modulus of the matrix.

Combining eqn (3) and (6)–(8), we come to the following equation for the dimensionless elastic energy:

$$\tilde{U}_n^{(\mathrm{el})}(\tilde{\xi}) = 2\pi \sum_{j=1}^{n} \left(\frac{\tilde{\xi}}{2} - 2 + \frac{\tilde{l}_\mathrm{r}}{2} - (\tilde{l} - 2)j \right)^2, \quad \tilde{\xi} = \frac{\xi}{a}. \tag{9}$$

The dimensionless elastic force, which resists the chains approaching, can be estimated as:

$$\tilde{F}_n^{(\mathrm{el})}(\tilde{\xi}) = -\frac{\mathrm{d}\tilde{U}_n^{(\mathrm{el})}(\tilde{\xi})}{\mathrm{d}\tilde{\xi}} = -\pi n\left(\tilde{\xi} - 2 - n\tilde{l}_\mathrm{r} + 2n\right). \tag{10}$$

III.2 Force of magnetic interaction between chains

In the dipole–dipole approximation, the force of the magnetic interaction between two n-particle chains, illustrated in Fig. 3, can be presented as:

$$F_n^{(m)}(\xi) = -\frac{3\mu_0}{2\pi} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{m_j(\xi) m_k(\xi)}{(\xi + 2a(j + k - 2))^4}. \tag{11}$$

Here μ_0 is the vacuum magnetic permeability; m_j is magnetic moment of the j-th particle in the chain (see Fig. 3); $\xi + 2a(j + k - 2)$ is the distance between centers of these particles.

Let us introduce the dimensionless magnetic force and particle magnetization in the following way:

$$\tilde{F}_n^{(m)}(\tilde{\xi}) = \frac{F_n^{(m)}(\tilde{\xi})}{Ea^2} = -\frac{8\pi\beta}{3} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\tilde{M}_j(\tilde{\xi}) \tilde{M}_k(\tilde{\xi})}{\left(\tilde{\xi} + 2(j + k - 2)\right)^4}$$
$$\tilde{M}_j = \frac{M_j}{M_\mathrm{s}}, M_j = \frac{m_j}{v_\mathrm{p}}, \beta = \frac{\mu_0 {M_\mathrm{s}}^2}{E}. \tag{12}$$

Here β is the parameter which defines the ratio of the energy of magnetic interaction between two magnetically saturated particles to the energy of elastic deformation of the matrix; M_j is magnetization of the j-th particle; M_s is saturated magnetization of the material particle.

The main problem now is to estimate the magnetic moment m_k of each particle of the interacting chains. We use here the main ideas of the approach,[14] successfully used for the determination of energy of interaction between two nonlinearly magnetizable particles. In the framework of this approximation, we assume that internal magnetic field $H_j^{(\mathrm{in})}$ inside the j-th particle of a chain is uniform. This field can be determined from the standard relation of the magnetostatics (see, for example, ref. 15):

$$H_j^{(\mathrm{in})} + \frac{M_j}{3} = H_0 + H_j^{(\mathrm{d})}. \tag{13}$$

Here H_0 is the field, external with respect to the chains (*i.e.* mean magnetic field inside the sample); $H_j^{(\mathrm{d})}$ is a uniform magnetic field, created by all particles of the chains in the place where the j-th particle is situated; M_j is the uniform magnetization of the j-th particle. In the framework of the dipole approximation, the field $H_j^{(\mathrm{d})}$ can be presented as (see Fig. 3):

$$H_j^{(\mathrm{d})}(\tilde{\xi}) = \frac{1}{16\pi a^3} \left[\sum_{k=1}^{n} \frac{m_k(1 - \delta_{jk})}{|k - j|^3} + \sum_{k=1}^{n} \frac{m_k}{\left(2(j + k - 2) + \tilde{\xi}\right)^3} \right]. \tag{14}$$

Here δ_{jk} is the Kronecker symbol. The first sum in the right part of (14) reflects the field, created by the particles of the same chain, in the place occupied by the j-th particle. The second sum corresponds to the field, created by the particles of the other chain. The relation (14) takes into account that, because of the symmetry, magnetic moments of the particles with the same number k in both the chains are identical.

We will determine the particle magnetization M_j by using the empirical Frohlich–Kennelly formula:[16,17]

$$M_j = \frac{\chi_\mathrm{p} M_\mathrm{s} H_j^{(\mathrm{in})}}{M_\mathrm{s} + \chi_\mathrm{p} H_j^{(\mathrm{in})}}, \ \tilde{M}_j = \frac{\chi_\mathrm{p} \tilde{H}_j^{(\mathrm{in})}}{1 + \chi_\mathrm{p} \tilde{H}_j^{(\mathrm{in})}}, \ \tilde{H}_j^{(\mathrm{in})} = \frac{H_j^{(\mathrm{in})}}{M_\mathrm{s}}. \tag{15}$$

Here χ_p is the initial susceptibility of the particle material.

Combining (13)–(15), we come to the system of n non-linear equations with respect to the dimensionless magnetization $\tilde{M}_j$ of all particles in the chains:

$$4\tilde{M}_j(\tilde{\xi}) \left(\frac{3}{\chi_\mathrm{p}\left(1 - \tilde{M}_j(\tilde{\xi})\right)} + 1 - \frac{2}{\left(4(j - 1) + \tilde{\xi}\right)^3} \right)$$
$$= 12\tilde{H}_0 + \sum_{k=1}^{n} \left[\tilde{M}_k(\tilde{\xi})(1 - \delta_{jk}) \left(\frac{1}{|j - k|^3} + \frac{8}{\left(2(j + k - 2) + \tilde{\xi}\right)^3} \right) \right],$$
$$j = 1, \ldots n. \tag{16}$$

Note that the dimensionless particle magnetization $\tilde{M}_j$ depends on the dimensionless distance $\tilde{\xi}$ between the chains. The system (16) has been solved numerically by using the Gauss–Seidel method.

Calculations of the force of interaction between two magnetizable particles are in good agreement with numerical solution of the same problem.[14] However, for the chains with many particles numerical solution of (16), therefore, determination of the force $\tilde{F}_n^{(m)}(\tilde{\xi})$, is cumbersome and inconvenient for practical use. That is why here we consider the reduced scheme, which allows us to estimate the magnetizations $\tilde{M}_j$ and the force (12) by using much more simple procedure.

In this scheme we will suppose that magnetic moments of all particles in the chains are identical and denote the moment of the particle in the n-particle chain as m_n.

Instead of the field (14), internal with respect to the j-th particle in the chain, we will introduce the field, averaged over

all possible numbers j of the particles in the chain:

$$h_n = \frac{1}{n}\sum_{j=1}^{n} H_j^{(\mathrm{d})} = \frac{m_n \Psi_n(\xi)}{16\pi n a^3},\ \Psi_n(\tilde{\xi})$$
$$= \sum_{j=1}^{n}\sum_{k=1}^{n}\left[\frac{1-\delta_{jk}}{|j-k|^3} + \frac{8}{\left(\tilde{\xi}+2(j+k-2)\right)^3}\right]$$
$$= 2\left[\sum_{i=1}^{n-1}\frac{n-i}{i^3} + 4\sum_{i=1}^{n}\frac{i}{\left(\tilde{\xi}+2(i-1)\right)^3}\right.$$
$$\left. + 4\sum_{i=1}^{n-1}\frac{i}{\left(\tilde{\xi}+2(2n-i-1)\right)^3}\right]. \quad (17)$$

By using the mean field h_n in (13) instead of the field (14), combining (13) and (17) with (15), we come to the following square equation with respect to the mean magnetization $\tilde{M}_n(\tilde{\xi})$:

$$\chi_{\mathrm{p}} f_n(\tilde{\xi})\tilde{M}_n^2(\tilde{\xi}) - G_n(\tilde{\xi})\tilde{M}_n(\tilde{\xi}) + \chi_{\mathrm{p}}\tilde{H}_0 = 0, \quad (18)$$

Eqn (18) has the following solution:

$$\tilde{M}_n(\tilde{\xi}) = \frac{G_n(\tilde{\xi}) - \sqrt{G_n^2(\tilde{\xi}) - 4\chi_{\mathrm{p}}^2\tilde{H}_0 f_n(\tilde{\xi})}}{2\chi_{\mathrm{p}} f_n(\tilde{\xi})}. \quad (19)$$

Note, that the relation under the root in (19) is always positive, therefore, the result for $\tilde{M}_n(\tilde{\xi})$ always has a physical meaning.

By using $m_n = M_n v_{\mathrm{p}}$ in eqn (11) instead of m_j and m_k, we get:

$$F_n^{(m)}(\xi) = -\frac{3\mu_0 m_n^2(\xi)}{2\pi}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{1}{(\xi+2a(j+k-2))^4}. \quad (20)$$

After simple mathematical transformation, we come to the following estimate of the dimensionless force of magnetic interaction between the chains:

$$\tilde{F}_n^{(m)}(\tilde{\xi}) = \frac{\pi\beta\tilde{M}_n^2(\tilde{\xi})}{9}\frac{\mathrm{d}\Psi_n(\tilde{\xi})}{\mathrm{d}\tilde{\xi}},\frac{\mathrm{d}\Psi_n(\tilde{\xi})}{\mathrm{d}\tilde{\xi}}$$
$$= -24\left(\sum_{i=1}^{n}\frac{i}{\left(\tilde{\xi}+2(i-1)\right)^4} + \sum_{i=1}^{n-1}\frac{i}{\left(\tilde{\xi}+2(2n-i-1)\right)^4}\right). \quad (21)$$

Parameter β is defined in eqn (12).

Some results of calculations of the magnetic force $\tilde{F}_n^{(m)}$ according to (12), (16) and (21) are shown in Fig. 4. The simple approximation (21) leads to a reasonable agreement with the more regular, but more cumbersome, approach (12) and (16).

III.3 The length of the stable chains

The total force, acting on each chain, illustrated in Fig. 3, can be presented as:

$$\tilde{F}_n(\tilde{\xi}, l_{\mathrm{r}}) = \tilde{F}_n^{(\mathrm{el})}(\tilde{\xi}, l_{\mathrm{r}}) + \tilde{F}_n^{(m)}(\tilde{\xi}). \quad (22)$$

Schematic dependence of $\tilde{F}_n(\tilde{\xi})$ on the distance $\tilde{\xi}$ is shown in Fig. 5 for different values of the applied field H_0. The negative sign of $\tilde{F}_n(\tilde{\xi})$ means that the magnetic attraction dominates the elastic forces, which resist the approach of the chains; the positive sign – shows that the elastic forces dominate.

Let us suppose that the field is increased. If the force $\tilde{F}_n(\tilde{\xi})$ is negative for all interchain distances $\tilde{\xi}$ (curve 1 in Fig. 5), the chains, with the given n, approach up to the dimensionless distance $\tilde{\xi} = 2$ (*i.e.* up to the physical contact between the particles at the chain extremities) and, as a result, form new twice longer chains. If the plot $\tilde{F}_n(\tilde{\xi})$ crosses the line $O\tilde{\xi}$ at some point $\tilde{\xi}_1 > 2$ (curves 3, 4), the chains approach to the distance $\tilde{\xi} > 2$. The cluster of chains, separated by the gap, cannot be considered as a whole chain. Thus the curve 2, which touches the axis $O\tilde{\xi}$ at the point $\tilde{\xi}_{\mathrm{cr}}$, corresponds to the threshold field $H_{\mathrm{a}}^{(n)}$ of aggregation of the n-particle chains. If the applied field $H_0 < H_{\mathrm{a}}^{(n)}$, the remote chains approach to some finite distance, but not amalgamate. If $H_0 > H_{\mathrm{a}}^{(n)}$, the n-particle chains aggregate and form $2n$ particle chains.

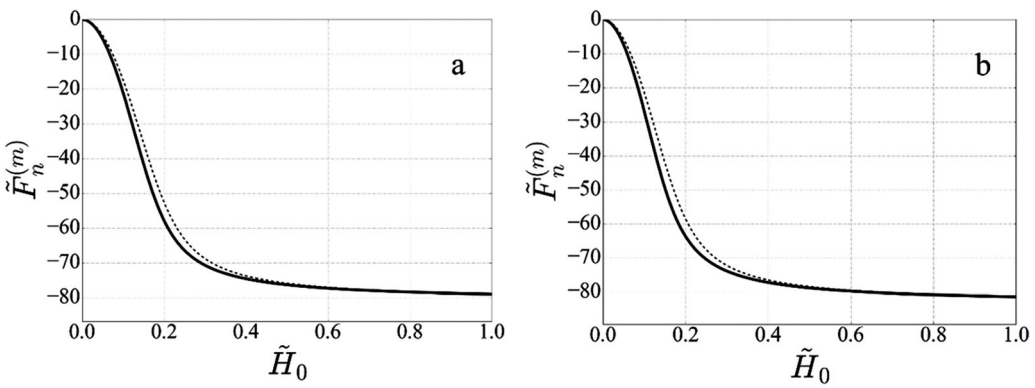

Fig. 4 The dimensionless force $\tilde{F}_n^{(m)}$ *vs.* the dimensionless magnetic field $\tilde{H}_0$ for different n. System parameters: $\tilde{\xi} = 2$ (the chains are in contact); parameter $\beta = 136$; initial susceptibility of the particle material $\chi_{\mathrm{p}} = 100$. Solid lines – magnetic force is calculated in the approximation (19) of identical moments in the chain; dashed ones – magnetic force is calculated in the approximation (16) where the magnetic moment of the particle depends on the number of that particle in the chain; *a* – $n = 2$; *b* – $n = 3$.

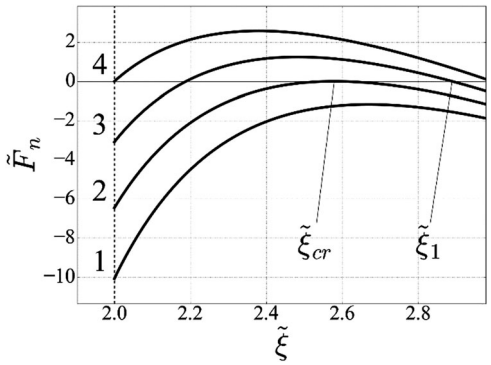

Fig. 5 Sketch of dependence of the force $\tilde{F}_n(\tilde{\xi})$ on the interchain distance $\tilde{\xi}$ for various magnitudes of the field H_0 at a given n, the same for all curves. The curves 1–4 – magnetic field is decreased.

The dimensionless threshold field $\tilde{H}_a^{(n)}$ as well as the dimensionless critical distance $\tilde{\xi}_{cr}$, which corresponds to amalgamation of the n-particle chains, can be found as a solution for the following system of equations:

$$\tilde{F}_n\left(\tilde{\xi}_{cr}, \tilde{H}_a^{(n)}, l_r\right) = 0, \frac{d\tilde{F}_n\left(\tilde{\xi}_{cr}, \tilde{H}_a^{(n)}, l_r\right)}{d\tilde{\xi}} = 0. \quad (23)$$

The analytical form for the field $\tilde{H}_a^{(n)}$ of the chain amalgamation can be obtained directly from the first equation of (23):

$$\tilde{H}_a^{(n)}(l_r) = \frac{\Phi_n\left(\tilde{\xi}_{cr}, l_r\right) + \left[1 + \chi_p f_n(2)\left(1 - \Phi_n\left(\tilde{\xi}_{cr}, l_r\right)\right)\right]\sqrt{\Phi_n\left(\tilde{\xi}_{cr}, l_r\right)}}{\chi_p\left(1 - \Phi_n\left(\tilde{\xi}_{cr}, l_r\right)\right)}, \quad (24)$$

$$\Phi_n\left(\tilde{\xi}, l_r\right) = -\frac{9\tilde{F}_n^{(el)}\left(\tilde{\xi}, l_r\right)}{\pi\beta\dfrac{d\Psi_n\left(\tilde{\xi}, l_r\right)}{d\tilde{\xi}}}.$$

Substituting (24) in the second equation of (23), we come to equation with respect to $\tilde{\xi}_{cr}$ at a given l_r. It allows us to get the final result for the field $\tilde{H}_a^{(n)}(l_r)$ of n-particle chains aggregation at the given initial distance l_r between the particles.

Now we are in a position to consider disintegration of the n-particle chains when the applied field is decreased. This chain can be considered as consisted of two $n/2$-particle chains with the distance $\tilde{\xi} = 2$ between centers of the particles at their extremities. The elastic force, which tends to rupture the $2n$-particle chain, dominates over the magnetic one, when the inequal $\tilde{F}_n(\tilde{\xi} = 2) > 0$ is held. Thus the criterion for the chain disintegration is:

$$\tilde{F}_n(2, \tilde{H}_d^{(n)}, l_r) = 0. \quad (25)$$

Solution of this equation allows us to determine the field $\tilde{H}_d^{(n)}$ of the chain disintegration:

$$\tilde{H}_d^{(n)}(l_r) = \frac{\Phi_n(2, l_r) + \left[1 + \chi_p f_n(2)(1 - \Phi_n(2, l_r))\right]\sqrt{\Phi_n(2, l_r)}}{\chi_p(1 - \Phi_n(2, l_r))}. \quad (26)$$

The function $f_n(\xi)$ is defined after eqn (18).

The fields $\tilde{H}_a^{(n)}(l_r)$ and $\tilde{H}_d^{(n)}(l_r)$ depend on the distance l_r which, with the equal probability, can have any value between $l_{min} = 2a$ and $l_{max}^{(n)} = 2n(l - 2a) + 2a$ (l is defined in eqn (1)). Let $l_{cr}^{(n)}$ be the value of l_r, corresponding to the aggregation or disaggregation of the n-particle chains when the applied field H_0 is increased or decreased respectively.

For the cases of increasing and decreasing fields the distance $l_{cr}^{(n)}$ can be found as a solution of the equations:

$$\tilde{H}_0 = \frac{\Phi_n\left(\tilde{\xi}_{cr}, l_{cr}^{(n)}\right) + \left[1 + \chi_p f_n(2)\left(1 - \Phi_n\left(\tilde{\xi}_{cr}, l_{cr}^{(n)}\right)\right)\right]\sqrt{\Phi_n\left(\tilde{\xi}_{cr}, l_{cr}^{(n)}\right)}}{\chi_p\left(1 - \Phi_n\left(\tilde{\xi}_{cr}, l_{cr}^{(n)}\right)\right)}. \quad (27)$$

and

$$\tilde{H}_0 = \frac{\Phi_n\left(2, l_{cr}^{(n)}\right) + \left[1 + \chi_p f_n(2)\left(1 - \Phi_n\left(2, l_{cr}^{(n)}\right)\right)\right]\sqrt{\Phi_n\left(2, l_{cr}^{(n)}\right)}}{\chi_p\left(1 - \Phi_n\left(2, l_{cr}^{(n)}\right)\right)}. \quad (28)$$

respectively.

The eqn (27) and (28) directly follow from eqn (24) and (26).

Let us denote the number of n-particle chains per unit volume of the system as g_n. This function must satisfy the following normalization condition:

$$\sum_{n=1}^{\infty} n g_n = \frac{\varphi}{v_p}. \quad (29)$$

which reflects conservation of the particles in the system after their aggregation. In order to determine g_n, we introduce a probability, $P^{(n)}$ that two n-particle chains have been united into the $2n$-one. In the framework of the used cell model, the initial (before their amalgamation), distance l_r with the equal probability lies in between $l_{min} = 2a$ and $l_{max}^{(n)} = 2n(l - 2a) + 2a$. The criterion for the chain aggregation reads $l_r < l_{cr}^{(n)}$, where $l_{cr}^{(n)}$ is determined from solution of eqn (27). Thus, the probability of the chain aggregation can be estimated as:

$$P^{(n)} = \begin{cases} \dfrac{l_{cr}^{(n)} - l_{min}}{l_{max}^{(n)} - l_{min}}, & \text{if} \dfrac{l_{cr}^{(n)} - l_{min}}{l_{max}^{(n)} - l_{min}} \le 1 \\ 1, & \text{if} \dfrac{l_{cr}^{(n)} - l_{min}}{l_{max}^{(n)} - l_{min}} > 1 \end{cases}. \quad (30)$$

Taking into account that the aggregation of two chains gives a chain with twice the number of particles, we get:

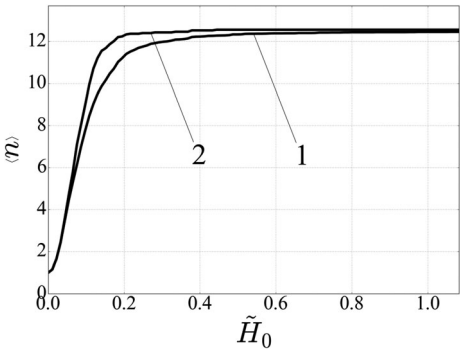

Fig. 6 Hysteresis of the mean particle number $\langle n\rangle$ in the chains *vs.* the dimensionless magnetic field $\tilde{H}_0$ line 1 – magnetic field is increased; line 2 – magnetic field is decreased. System parameters: concentration of the particles φ = 0.30; elastic modulus of the matrix E = 20 kPa; saturated magnetization of the particle material M_s = 1470 kA m^{-1}; initial susceptibility of the particle material χ_p = 100.

$$g_1 = \frac{\varphi}{v_p}\left(1 - P^{(1)}\right), \quad g_2 = \frac{\varphi}{2v_p}\left(1 - P^{(2)}\right)P^{(1)},$$
$$g_4 = \frac{\varphi}{4v_p}\left(1 - P^{(4)}\right)P^{(1)}P^{(2)}, \ldots, \tag{31}$$
$$g_{2^k} = \frac{\varphi}{2^k v_p}\left(1 - P^{(2^k)}\right)\prod_{i=0}^{k-1} P^{(2^i)}.$$

Analysis shows that the functions (31) satisfy to the normalization conditions (29).

Similar considerations lead to the same relations (30) and (31) for the situation with the chain disintegrating when the field is decreased. The only difference is that at the decreasing field the critical distance $l_{cr}^{(n)}$ must be determined as a solution of eqn (28).

The plots, presented in Fig. 5, show that $\tilde{H}_d^{(2n)} < \tilde{H}_a^{(n)}$, *i.e.* disintegration of the 2*n*-particle chain takes place at a smaller field than the field corresponding to the chain appearance. Converting $\tilde{H}_d^{(2n)}$ as function of n, we get the number of the particles in the stable chain when the applied field $\tilde{H}_0$ is decreased.

Knowing the distribution function g_n, we can easily calculate the mean particle number $\langle n\rangle$ in the chains:

$$\langle n\rangle = \frac{\sum_{n=1}^{\infty} n g_n}{\sum_{n=1}^{\infty} g_n} = \frac{\varphi}{v_p \sum_{n=1}^{\infty} g_n}. \tag{32}$$

Some results of calculations of the mean number $\langle n\rangle$ are shown in Fig. 6. Obviously the hysteretic dependence of the chain length on the magnetic field must lead to the hysteretic dependences of macroscopical properties of the system.

IV. Results and discussion

By using simplified (21) and (22) with the identical magnetization M_n for all particles in the chain, we get the following relations for the composite mean magnetization:

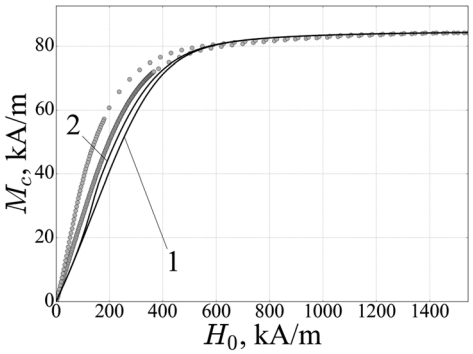

Fig. 7 The hysteresis of the magnetization of the composite. Particle concentration φ = 0.058, the other parameters of the system are the same as in Fig. 6. Gray circles – experimental; solid lines –theory. Lines 1 and 2 – magnetic field is increased and decreased respectively.

$$M_c = \frac{\sum_{n=1}^{\infty} M_n g_n}{\sum_{n=1}^{\infty} g_n} = \frac{v_p\langle n\rangle}{\varphi}\sum_{n=1}^{\infty} M_n g_n. \tag{33}$$

Some results of calculations of the curves of the composite magnetizations as well as results of measurements of M_c in the performed experiments, are shown in Fig. 7 and 8.

Results of calculation of the composite magnetic susceptibility $\chi_c = M_c/H_0$ as well as the experimental results for this magnitude are given in Fig. 9 and 10.

In spite of simplicity of the model, the theoretical curves, presented in Fig. 7–10, reproduce the main physical features of the experimental results – the hysteretic behavior of magnetization and susceptibility as well as the maxima of susceptibility at the moderate magnitudes of the applied field. The quantitative deviation of the theoretical results from the experimental ones can be explained by the model simplification of neglect of the mutual magnetization of the particles in the different chains. As well known, the mutual magnetization of the particles enhances effective susceptibility of magnetic composites. However, account of these effects makes the calculations and the final results much more cumbersome. That is why here, to concentrate on the effect of the particles chaining in the elastic medium and the hysteresis phenomenon, we have restricted

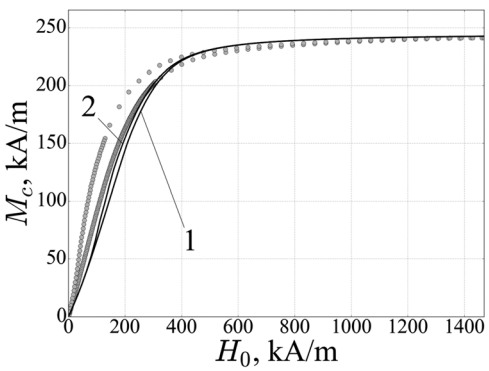

Fig. 8 Same as in Fig. 7 when the particle concentration φ = 0.167.

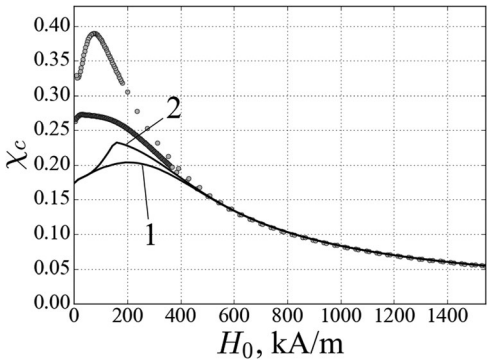

Fig. 9 The hysteresis of the magnetic susceptibility of the composite. Concentration φ = 0.058. Other parameters of the system are the same as in Fig. 6. Lines 1 and 2 – magnetic field is increased and decreased respectively.

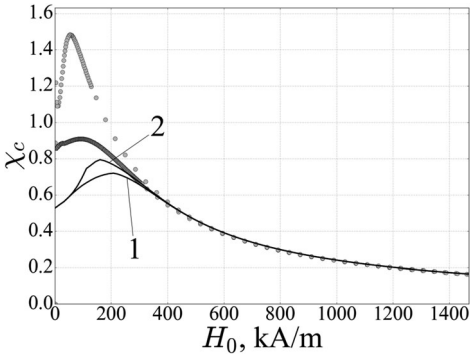

Fig. 10 Same as in Fig. 9 for concentration φ = 0.167.

ourselves by the simplest approximation of the mutual magnetization of the nearest aggregating chains only.

One cannot exclude also that in the experiments some particles, at the stage of the composite synthesis, have formed doublets and other clusters, which are not taken into account in the present model of the initial gas-like distribution of the single particles. Analysis shows that the presence of the clusters can pronouncedly enhance the composite magnetization.

Generalization of the proposed approach taking into account the effect of the collective mutual magnetization of the chains as well as their possible initial agglomeration can be considered as a natural continuation of this work.

V. Conclusion

Experimental study of magnetic properties of soft magnetic gels with embedded micron-sized magnetizable particles demonstrate hysteretic dependences of the composite magnetization on the applied magnetic field; the composite susceptibility non-monotonic, with maximum, depends on the field. These features are explained theoretically on the basis of conception of the unification of particles into linear chain-like aggregates. Analysis shows that macroscopic properties of the composites are determined by the size of the chains. In its turn, dependence of this size on the applied field has the hysteretic character, which leads to the hysteretic dependences of the magnetization and susceptibility on the applied field.

The initial increase of the composite susceptibility, with the applied field, is explained by chaining of the particles and the fact that demagnetizing factor of the chain decreases with its length. A further increase of the field leads to saturation of the magnetization of the particles and, as a consequence, to a decrease of the composite susceptibility. The competition between effects of decrease of the demagnetizing factor of chains, on the one hand, and decrease of the particle susceptibility, on the other hand, is the physical cause of the maxima of the composite susceptibility.

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